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Nanocomposites for Enhanced Structural Integrity

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Executive Summary

The main objective of the proposed research was to develop the science base necessary for full utilization of nanoreinforcements into polymers and fiber composites to improve mechanical, thermal and electrical properties. Two types of nanoreinforcements were studied: 0-dimensional SiC nanoparticles and 2-dimensional graphite nanoplatelets.

As property improvements are possible only when the nanoreinforcements are uniformly dispersed in and well bound to the polymer matrix, the emphasis was on developing methods to optimally functionalize these nanoreinforcements. Both a coupling agent and a dispersant were used to improve the processing and properties of SiC/vinyl ester nanocomposite. A coupling agent methacryloxy propyl trimethoxy silane (MPS) was found to be effective for the SiC nanocomposite. As for the graphite nanoplatelets, the effects of the following parameters on properties were investigated: size reduction through vibratory milling, thickness reduction through intercalation/expansion/exfoliation, and oxidation through nitric acid treatment. The most effective parameter was found to be the proper oxidation by acid treatment.

Material properties studied were tensile strength and modulus, flexural strength and modulus, thermal conductivity, and electrical conductivity. The effects of adding GNPs into fiber composites as well as of using thinner prepreg plies were also studied to a limited extent. The properly oxidated GNPs were found to improve not only mechanical properties but also thermal and electrical properties of GNP/epoxy nanocomposites.

Researchers

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Publications in Journals

- J-1. V. Yong and H.T. Hahn, "Processing and Properties of SiC/Vinyl Ester Nanocomposites," *Nanotechnology*, Vol. 14, 2004, pp.1338-1343.
- J-2. L.M. Viculis, J.J. Mack, O.M. Mayer, H.T. Hahn, and R.B. Kaner, "Intercalation and Exfoliation Routes to Graphite Nanoplatelets," *Journal of Materials Chemistry*, Vol. 15, 2005, pp. 974-978.
- J-3. V. Yong and H.T. Hahn, "Dispersant Optimization Using Design of Experiments for Sic/Vinyl Ester Nanocomposites," *Nanotechnology*, Vol. 16, 2005, pp. 354-360.

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- J-4. J.J. Mack, L.M. Viculis, A. Ali, R. Luoh, G. Yang, H.T. Hahn, F.K. Ko, and R.B. Kaner, "Graphite Nanoplate Reinforcement of Electrospun Polyacrylonitrile Nanofibers," *Advanced Materials*, Vol. 17, 2005, pp. 77-80.
- J-5. V. Yong and H.T. Hahn, "Rheology of SiC/Vinyl Ester Nanocomposites," *Journal of Applied Polymer Science*, Vol. 102, 2006, pp. 4365-4371.
- J-6. M.T. Hung, O. Choi, Y.S. Ju, and H.T. Hahn, "Heat Conduction in Graphite-Nanoplatelet-Reinforced Polymer Nanocomposites," *Applied Physics Letters*, Vol. 89, 2006, 023117.
- J-7. V. Yong and H.T. Hahn, "Moisture Absorption Modeling Using Design of Experiments," *Journal of Applied Polymer Science*, Vol. 103, 2007, pp. 1539-1543.
- J-8. H. Kim, H.T. Hahn, L.M. Viculis, S. Gilje, and R.B. Kaner, "Electrical Conductivity Of Graphite/Polystyrene Composites Made From Potassium Intercalated Graphite," *Carbon*, Vol. 45, 2007, pp. 1578-1582.

Publications in Conference Proceedings

- C-1. J. Mack, L. Viculis, A. Ali, R. Luoh, G. Yang, R. Kaner, H.T. Hahn, and F. Ko, "Graphite Nanoplatelet Based Nanocomposites by the Electrospinning Process," *Proc. American Society for Composites, 17th Technical Conference* (CD-ROM), Oct. 2002.
- C-2. R. Luoh, F. Ko and H.T. Hahn, "Low Dielectric Constant Electrospun Nanocomposite Fiber Mats Produced by Electrospinning," *Proc. 14th Int. Conf. on Composite Materials* (CD-ROM), July 2003.
- C-3. J.-Y. Kim, L. Yu and H.T. Hahn, "Graphite Nanoplatelet/Epoxy Vinyl Ester Composites," *Proc. 14th Int. Conf. on Composite Materials* (CD-ROM), July 2003.
- C-4. L. Viculis, J. Mack, A. Ali, R. Luoh, G. Yang, R. Kaner, T. Hahn, and F. Ko, "Nanocomposite Fibrils from Graphite Nanoplatelets," *Proc. 14th Int. Conf. on Composite Materials* (CD-ROM), July 2003.
- C-5. V. Yong and H.T. Hahn, "Kevlar/Vinyl Ester Composites with SiC Nanoparticles," *SAMPE 2004 Proc.* (CD ROM), May 2004.
- C-6. M. Lui and H.T. Hahn, "Nanoparticle-Based Mitigation of fiber Print-Through in Composite Mirrors," *Proc. American Society for Composites, 20th Technical Conference* (CD ROM), Sept. 2005.
- C-7. Choi, H.T. Hahn, S. Gilje, and R.B. Kaner, "Graphite Nanoplatelet Reinforced Epoxy Composites: The Effect of Exfoliation and Surface Treatment," *SAMPE ISTC Vol. 37* (CD ROM), Oct. 2005.
- C-8. K. Yamaguchi and H.T. Hahn, "The Improved Ply Cracking Resistance of Thin-Ply Laminates," *Proc. 15th Int. Conf. on Composite Materials* (CD-ROM), June 2005.
- C-9. L. Sasa, H.T. Hahn and J. Higgins, "Effect of Graphite Nanoplatelet Loading on the Microcrack Mitigation Capabilities of Composite Structures," *AIAA-2005-2151, AIAA 46th SDM Conference*, April 2005.
- C-10. Choi, S. Gilje, H.T. Hahn, and R.B. Kaner, "Graphite Nanoplatelet Composites," *SAMPE 2006 Proc.* (CD ROM), May 2006.
- C-11. S. Gilje, O. Choi, R.B. Kaner, and H.T. Hahn, "Graphite Particle Size Effects on Mechanical Properties of Epoxy Composites," *SAMPE 2006 Proc.* (CD ROM), May 2006.
- C-12. H. Kim, H.T. Hahn, L.M. Viculis, and R.B. Kaner, "Graphite Nanoplatelet (GNP)/Polymer Nanocomposites based on Potassium-Benzene-Intercalation Compounds," *Proc. American Society for Composites, 21st Technical Conference* (CD ROM), Sept. 2006.

Dissertations

Lisa Viculis, "Intercalation and Exfoliation of Layered Materials to Produce Nanoplatelets and Nanoscrolls," Ph.D. thesis, Chemistry and Biochemistry, UCLA, 2004.

M. Luis, "Improving Surface Quality of Composite Mirror Using Nanoparticles," M.S. Thesis, Mechanical and Aerospace Engineering, UCLA, 2005.

O. Choi, "Graphite Nanoplatelet Composites," M.S. Thesis, Mechanical and Aerospace Engineering, UCLA, 2005.

V. Yong, "Nano-Particulate Dispersion and Reinforcement of Nanostructured Composite Materials, Ph.D. Thesis, Materials Science and Engineering, UCLA, 2005

Objectives

The main objective of the proposed research was to develop the science base necessary for full utilization of nanoreinforcements into polymers and fiber composites to improve mechanical, thermal and electrical properties. Two types of nanoreinforcements were studied: 0-dimensional SiC nanoparticles and 2-dimensional graphite nanoplatelets (GNPs). The SiC nanoparticles had a nominal diameter of 30 nm while the graphite nanoplatelets had a nominal thickness of about 100 nm.

Technical Approach

As property improvements are possible only when the nanoreinforcements are uniformly dispersed in and well bound to the polymer matrix, the emphasis was on developing methods to optimally functionalize these nanoreinforcements. Both a coupling agent and a dispersant were used to improve the processing and properties of SiC/vinyl ester nanocomposites. As for the graphite nanoplatelets, the effects of the following parameters on properties were investigated: size reduction through vibratory milling, thickness reduction through intercalation, expansion and exfoliation, and oxidation through nitric acid treatment.

Material properties studied were tensile strength and modulus, flexural strength and modulus, thermal conductivity, and electrical conductivity. The effects of adding GNPs into fiber composites as well as of using thinner prepreg plies were also studied to a limited extent.

Summary and Conclusions

Results from the project have been published in archival journals and conference proceedings. Abstracts of these publications are included in this section.

It has been found that the MPS coupling agent can improve dispersion of SiC nanoparticles in a vinyl ester resin and increase the mechanical properties of the resulting composite. The applicability of the same coupling agent to other oxide nanoparticles requires further investigation.

The GNPs can increase mechanical properties and conductivities of their epoxy-matrix composites when properly oxidized via acid treatment. However, an optimized combination of exfoliation and surface functionalization requires further study.

Journals

- J-1. V. Yong and H.T. Hahn, "Processing and Properties of SiC/Vinyl Ester Nanocomposites," *Nanotechnology*, Vol. 14, 2004, pp.1338-1343.

The feasibility of improving polymer composites was investigated using 30 nm SiC nanoparticles in a vinyl ester resin. Even when the particle loading was less than 4% by weight, the viscosity of the nanoparticle suspension was found to increase much higher than that of microparticle suspension. This phenomenon may be the result of association between

nanoparticles and polymer molecules, effectively making the nanoparticles larger. The resulting reduction in the mobility of polymer molecules also led to delayed curing. Ultrasonic mixing did not fully disperse the particles. As a result, the composite strength did not improve although the modulus increased. The use of a dispersant, methacryloxy propyl trimethoxy silane (MPS), improved the dispersion quality and hence the composite strength. The paper discusses the issues involved with processing, characterization and properties of SiC/vinyl ester nanocomposites. Methods of improving the nanocomposite quality are proposed in the paper as well.

- J-2. L.M. Viculis, J.J. Mack, O.M. Mayer, H.T. Hahn, and R.B. Kaner, "Intercalation and Exfoliation Routes to Graphite Nanoplatelets," *Journal of Materials Chemistry*, Vol. 15, 2005, pp. 974-978.

Graphite nanoplatelets with thicknesses down to 2–10 nm are synthesized by alkali metal intercalation followed by ethanol exfoliation and microwave drying. Graphite that has already been intercalated and exfoliated with an oxidizing acid is reintercalated with an alkali metal to form a first stage compound, as confirmed by powder X-ray diffraction. This can be achieved either by heating graphite and potassium or cesium at 200° C, or at room temperature using a sodium–potassium alloy. Reaction of the intercalated graphite with ethanol causes exfoliation of the graphene layers. Microwave radiation aids in drying and results in further separation of the sheets. Thermogravimetric analysis indicates that the graphite nanoplatelets are approximately 150° C less stable in air than pristine graphite. High aspect ratio graphite nanoplatelets offer promise as reinforcements for high strength carbon–carbon composites.

- J-3. V. Yong and H.T. Hahn, "Dispersant Optimization Using Design of Experiments for SiC/Vinyl Ester Nanocomposites," *Nanotechnology*, Vol. 16, 2005, pp. 354-360.

The effect of dispersants on particle dispersion and flexural properties of SiC/vinyl ester nanocomposites was studied by factorial and response surface designs. The results show that the coupling agent '*gamma*-methacryloxy propyl trimethoxy silane (MPS)' has no adverse side effect on the flexural properties as illustrated by the good correlation between maximizing the flexural strength and minimizing the agglomerates. However, the dispersant 'BYK-W966' has a slight adverse side effect on the flexural properties although it improves dispersion at higher dosage. With an optimal dosage of MPS and W966, a small amount of SiC in 0.5 wt% results in 8% increase in strength and 14% increase in modulus. The flushing operation using the dispersant '1-octanol/decane' achieves an excellent SiC dispersion but it does not result in improved flexural properties. This confirmed that a better state of nanoparticle dispersion does not necessarily lead to improved flexural properties. A good dispersion coupling with a strong filler/matrix interfacial bonding is the key to obtain enhanced flexural properties.

- J-4. J.J. Mack, L.M. Viculis, A. Ali, R. Luoh, G. Yang, H.T. Hahn, F.K. Ko, and R.B. Kaner, "Graphite Nanoplate Reinforcement of Electrospun Polyacrylonitrile Nanofibers," *Advanced Materials*, Vol. 17, 2005, pp. 77-80.

Graphite nanoplatelets have been synthesized via an intercalation/exfoliation process. Reinforced polymer composites are formed by adding 1-4% graphite nanoplatelets to a PAN solution. Electrospinning produces nanofibers with average diameters of 300 nm. Selected area

electron diffraction reveals the presence of crystalline graphite within the amorphous-polymer nanofiber matrix. The composite nanofibers demonstrate a modest increase in thermal stability with increasing weight-percent graphite nanoplatelets. Nanohardness measurements using AFM indicate that the nanoplatelets can serve as an alternative reinforcement material since the Young's modulus doubles with only 4 wt.-% incorporation of graphite nanoplatelets.

- J-5. V. Yong and H.T. Hahn, "Rheology of SiC/Vinyl Ester Nanocomposites," *Journal of Applied Polymer Science*, Vol. 102, 2006, pp. 4365-4371.

Silicon carbide (SiC) nanoparticles with no surface treatment raise the viscosity of a vinyl ester resin much more intensely than micrometer-size SiC particles. An effective dispersant generally causes a reduction in the resin viscosity attributed to its surface-active properties and thereby increases the maximum fraction of particles that can be introduced. This article assesses the rheological behavior of SiC-nanoparticle-filled vinyl ester resin systems with the Bingham, power-law, Herschel–Bulkley, and Casson models. The maximum particle loading corresponding to infinite viscosity has been determined to be a 0.1 volume fraction with the $(1 - \eta_r^{-1/2}) - \phi$ dependence (where η_r is the relative viscosity and ϕ is the particle volume fraction). The optimum fractional weight percentage of the dispersants (wt % dispersant/wt % SiC) is around 40% for 30-nm SiC nanoparticles, which is much higher than 1–3% for micrometer-size particles. SiC nanoparticles at a concentration of 9.2 wt % (0.03 volume fraction) cause a fourfold increase in the resin viscosity. The addition of a dispersant at the optimum dosage lowers the viscosity of SiC/vinyl ester suspensions by 50%. The reduction in the viscosity is substantial to improve the processability of SiC/vinyl ester nanocomposites.

- J-6. M.T. Hung, O. Choi, Y.S. Ju, and H.T. Hahn, "Heat Conduction in Graphite-Nanoplatelet-Reinforced Polymer Nanocomposites," *Applied Physics Letters*, Vol. 89, 2006, 023117.

Heat transport in polymer nanocomposites reinforced with graphite nanoplatelets (GNPs) is studied using high-precision thermal conductivity measurements. The resistance to heat conduction across interfaces between GNPs and the polymer matrix has a strong effect on energy transport in the nanocomposites. The thermal conductivity is observed to increase when GNPs are pretreated with nitric acid to improve interfacial bonding. The improvement in the thermal conductivity, however, is much smaller than the corresponding improvement in mechanical properties. The thermal interface resistance extracted from the present thermal conductivity data is comparable to that obtained from the previously reported data on carbon nanotube suspensions.

- J-7. V. Yong and H.T. Hahn, "Moisture Absorption Modeling Using Design of Experiments," *Journal of Applied Polymer Science*, Vol. 103, 2007, pp. 1539-1543.

The effect of temperature and humidity on equilibrium moisture content of laminates was studied by response surface design. Two glass fabric-reinforced laminated composite materials with different epoxy matrix resins, laminates A and B, were studied. Laminates A and B used are cyanate ester and polyphenylene oxide modified epoxy based laminate, respectively. The results show that the response surface profiles of moisture absorption for the two laminate materials are similar though their amounts of moisture absorption are different. The temperature-humidity

interaction effect and the quadratic effect of temperature are significant for laminate A. However, only the linear effects of temperature and humidity are significant for laminate B. Predictive models relating the important factors to the equilibrium moisture content were proposed in the paper. The models developed can be used to predict and assess the reliability of the laminates for moisture related failures.

- J-8. H. Kim, H.T. Hahn, L.M. Viculis, S. Gilje, and R.B. Kaner, "Electrical Conductivity Of Graphite/Polystyrene Composites Made From Potassium Intercalated Graphite," *Carbon*, Vol. 45, 2007, pp. 1578-1582.

Composites between graphite and polystyrene have been synthesized starting from potassium intercalated graphite and styrene vapor. This in situ polymerization process can be used to make electrically conductive composites containing well-dispersed thin graphite sheets. The conductivities of the composites increase as the number of ordered carbon layers increases. With only 10% graphite in a polystyrene matrix, an electrical conductivity up to $1.3 \cdot 10^{-1}$ S/cm can be obtained. The key is synthesizing a material with at least four ordered graphite layers (a stage IV complex) separated by polystyrene. This composite shows an improvement in conductivity over a control composite made by radical polymerization of styrene containing the same amount of dispersed graphite which had a conductivity of $5.0 \cdot 10^{-3}$ S/cm. Characterization of the complexes by powder X-ray diffraction, scanning electron microscopy and electrical conductivity is presented.

Conference Proceedings

- C-1. J. Mack, L. Viculis, A. Ali, R. Luoh, G. Yang, R. Kaner, H.T. Hahn, and F. Ko, "Graphite Nanoplatelet Based Nanocomposites by the Electrospinning Process," *Proc. American Society for Composites, 17th Technical Conference* (CD-ROM), Oct. 2002.

Graphite nanoplatelets are produced by a chemical route using a low energy intercalation/exfoliation process providing an alternative pathway to nanomaterials. In this process, graphite is heated to 200 °C in the presence of potassium to form the first stage intercalation compound, KC_8 . Exfoliation in ethanol then creates a dispersion of carbon nanosheets. In a previous study, it has been shown that single-walled carbon nanotubes (SWNT) can be dispersed in polymer solutions to form nanocomposite fibrils by the electrospinning process. In order to achieve orientation and to facilitate processing and assessment of the engineering properties of the nanosheets, the graphite nanoplatelets were dispersed in 7 wt. % polyacrylonitrile (PAN) in N,N Dimethylformamide (DMF) solution to form nanoscale fibrils by the electrospinning process. The composite fibrils were characterized by Dynamic Light Scattering (DLS), Thermogravimetric Analysis (TGA), Scanning Electronic Microscopy (SEM), Transmission Electron Microscopy (TEM), and Atomic Force Microscopy (AFM) for samples consisting of 1-4 wt. % of graphite nanoplatelets.

- C-2. J.-Y. Kim, L. Yu and H.T. Hahn, "Graphite Nanoplatelet/Epoxy Vinyl Ester Composites," *Proc. 14th Int. Conf. on Composite Materials* (CD-ROM), July 2003.

Graphite nanoplatelets (GNP) are expected to be a better reinforcement choice to polymers than carbon nanotubes because the former has the same reinforcement efficiency in 2 directions. In the present work, as-received nanoplatelets were mixed with an epoxy vinyl ester resin to study their reinforcement efficiency. The as-received GNPs had an average thickness of 20 nm. The GNP volume content was varied from 0 to 12 %. As expected, the modulus increased with increasing GNP volume content. However, the flexural strength decreased when the GNP volume exceeded 2 %. The observed increase in the modulus was much less than expected from micromechanics predictions based on a large aspect ratio. One of the reasons for such low modulus is that the measured average aspect ratio is only about 100 whereas an optimum aspect ratio is in the range of 1000. Percolation was observed around 2.5 vol% GNP to yield an electrical conductivity of 10^{-8} S/cm. Thus, the as-received GNPs can be used to improve electrical conductivity without sacrificing strength. However, further performance improvements are possible if individual graphene sheets can be separated from the as-received GNPs.

- C-3. L. Viculis, J. Mack, A. Ali, R. Luoh, G. Yang, R. Kaner, T. Hahn, and F. Ko, "Nanocomposite Fibrils from Graphite Nanoplatelets," *Proc. 14th Int. Conf. on Composite Materials* (CD-ROM), July 2003.

This paper introduces a new reinforcement form for nanocomposites. Graphite nanoplatelets are produced by a chemical route using a low energy intercalation/exfoliation process providing an alternative, low cost pathway to nanomaterials. In this process, graphite is heated to 200 °C in the presence of potassium to form the first stage intercalation compound, KC_8 . Exfoliation in ethanol then creates a dispersion of graphitic sheets. In a previous study, it has been shown that single-walled carbon nanotubes (SWNT) can be dispersed in polymer solutions to form nanocomposite fibrils by the electrospinning process. In order to achieve orientation and to facilitate processing and assessment of the engineering properties of the nanosheets, the graphite nanoplatelets were dispersed in a 7 wt. % polyacrylonitrile (PAN) solution in N,N Dimethylformamide (DMF) to form nanoscale fibrils by the electrospinning process. The composite fibrils were characterized by Thermogravimetric Analysis (TGA), Scanning Electronic Microscopy (SEM), Transmission Electron Microscopy (TEM), and Atomic Force Microscopy (AFM) for samples consisting of 1-4 wt. % of graphite nanoplatelets (GNP).

- C-4. V. Yong and H.T. Hahn, "Kevlar/Vinyl Ester Composites with SiC Nanoparticles," *SAMPE 2004 Proc.* (CD ROM), May 2004.

Kevlar/vinyl ester composites with SiC nanoparticles were fabricated using hand lay-up. Vacuum and mechanical press were used to suppress porosity, increase the fiber volume fraction and assist infiltration. The SiC nanoparticles were examined using TEM and TGA, and were vacuum-baked at 2000C to remove adsorbed moisture, as per TGA measurement. *Gammamethacryloxy propyl trimethoxy silane* (MPS) was chosen as the coupling agent and its dosage was calculated to achieve monolayer coverage. Both mixing routes with (1) the nanoparticles pretreated with a dilute MPS solution in an acid 5% (v/v) water-ethanol mixture and (2) the MPS sonicated as an integral blend with the filled vinyl ester, were attempted. FTIR was used to study the silanol condensation between MPS and the SiC nanoparticles. X-ray inspection and cross-sectioning were performed on the nanocomposite panels. The modulus from

3-point bend tests showed an increase for both mixing routes, whereas strength increased for route (2) but decreased for route (1). The increases in modulus and strength are likely attributed to the better dispersion quality as observed under the optical microscope and AFM, lower resin viscosity, lower porosity, and a stronger coupling/bonding between the SiC nanoparticles and vinyl ester resin as a result of the MPS addition. The decrease in strength in route (1) was likely caused by the siloxane layer between the SiC nanoparticles associated with the three reactive silanols per molecule of MPS. A 19% increase in tensile strength was found in route (2) with 1 vol. % SiC addition, which confirmed the high potential of nanoparticles in enhancing the mechanical properties of structural composites.

- C-5. M. Lui and H.T. Hahn, "Nanoparticle-Based Mitigation of fiber Print-Through in Composite Mirrors," *Proc. American Society for Composites, 20th Technical Conference* (CD ROM), Sept. 2005.

A composite mirror based on carbon fiber reinforced polymer would have significant weight savings over a conventional mirror because of its lower density. However, it has been difficult to achieve a surface quality comparable to that of a conventional mirror because of fiber print-through. The heterogeneity inherent in composite manifests itself in the form of undulations on the mirror surface. The present paper describes how the surface quality of a composite mirror can be improved through the addition of nanoparticles. As fiber print-through is a result of difference in shrinkage between matrix and fibers during curing, providing a resin-rich region near the surface can annihilate uneven shrinkage. However, maintaining a resin-rich surface is not easy because the extra resin can easily be squeezed out during curing. Fortunately, the addition of alumina nanoparticles into the resin layer has been found to preserve the resin-rich surface region. Atomic force microscopy (AFM) results show a substantial decrease in surface roughness as 1 vol% of nanoparticles is dispersed into the surface resin layer. With 2 vol% addition of nanoparticles, the resulting mirror surface is already of the same smoothness as the glass mandrel surface itself. Thus, no further improvement is observed as more nanoparticles are added. Finite element analyses of the observed cross sections also indicate the disappearance of fiber print-through with the formation of a resin-rich region near the surface.

- C-6. O. Choi, H.T. Hahn, S. Gilje, and R.B. Kaner, "Graphite Nanoplatelet Reinforced Epoxy Composites: The Effect of Exfoliation and Surface Treatment," *SAMPE ISTC Vol. 37* (CD ROM), Oct. 2005.

The successful development of nanocomposites requires the reinforcement phase to have a high aspect ratio and good bonding with the matrix resin. As a first step toward this goal, potassium and benzene are sequentially intercalated into commercially available GNPs to increase the aspect ratio by exfoliation. The resulting graphite intercalation compounds (GICs) are treated in three different ways to prepare their surfaces for improved bonding: washing in alcohol to improve wetting, cryogenic treatment to roughen the surface, and nitric acid immersion to oxidize the surface. The treated GICs are dispersed in Epon 862 resin with Epicure-W curing agent using a shear mixer followed by sonication. The GNP volume fraction is maintained at 1%. The best improvements are observed with KC₄₈/benzene compound treated with nitric acid although all composites perform better than the neat epoxy. Compared with the neat epoxy, the Young's modulus increases 97%, the strength 65%, and the electrical conductivity from 10⁻¹² to

10^{-4} S/cm. The results so far indicate that GNPs with proper intercalation/exfoliation and surface treatment offer a great potential to improve mechanical and electrical properties of the resulting composites. The low cost of GNPs also makes their commercial applications much more viable.

- C-7. K. Yamaguchi and H.T. Hahn, "The Improved Ply Cracking Resistance of Thin-Ply Laminates," *Proc. 15th Int. Conf. on Composite Materials* (CD-ROM), June 2005.

In multidirectional laminates, matrix/interface cracks occur in plies with fibers not parallel to the loading much before final failure. A toughened resin is generally used to improve the resistance to such ply cracking. Another approach, however, is to use thinnest plies possible. The difficulty with the latter approach is the fabrication of thinner plies than currently available. Recently, prepregs much thinner than conventional ones have become available [1, 2]. The laminates fabricated with these thin plies were shown to be able to eliminate ply cracking almost up to the final laminate failure under static loading. Such improvements in ply cracking resistance are in line with predictions by a combination of a stress criterion and an energy criterion. This paper shows how much improvements can be obtained in ply cracking resistance under tensile static and fatigue loading using both a replication technique and electrical resistance measurements. It also presents a model to predict the crack density as a function of fatigue cycles using the energy criterion.

- C-9. L. Sasa, H.T. Hahn and J. Higgins, "Effect of Graphite Nanoplatelet Loading on the Microcrack Mitigation Capabilities of Composite Structures," AIAA-2005-2151, *AIAA 46th SDM Conference*, April 2005.

Graphite nanoplatelets were added to the matrices of carbon fiber/epoxy composites to determine the effect of particle loading on the microcrack mitigation capabilities of composite samples after exposure to cryogenic temperatures. Particle volume percents of zero, one, two, three, four, five, and ten were added to the epoxy resin during filament winding. Although most of the samples contained some microcracks after cryogenic cycling, the graphite nanoplatelets seemed to have prevented the microcracks from propagating further. After comparing the various graphite nanoplatelet loadings, the addition of ten volume percent demonstrated the most drastic decrease in the number of microcracks within the laminate.

- C-10. O. Choi, S. Gilje, H.T. Hahn, and R.B. Kaner, "Graphite Nanoplatelet Composites," *SAMPE 2006 Proc.* (CD ROM), May 2006.

Graphite nanoplatelets (GNPs) were studied as reinforcement in epoxy resins due to their high aspect ratio. GNPs are of particular interest as a reinforcing filler material because of their high mechanical strength and electrical conductivity. In addition, the structure of GNP particles could enable simplified processing because of the ease of exfoliation given the weak c-axis bonding between the layers in graphite. We have investigated the possibility of significant electrical and mechanical property enhancement by using a low volume fraction (1 vol%) of GNPs. For the first trials, the potassium graphite intercalation compound (K-GIC) was exposed to ethyl and methyl alcohol co-intercalants. This was followed by three different methods of drying to induce exfoliation: furnace, oven and microwave heating. In separate experiments, the 4th stage potassium intercalated graphite (KC₄₈) was exposed to benzene to form a K-GIC-benzene ternary

compound. The mechanical properties were measured in three point flexural tests. The electrical conductivity of the samples was also measured.

- C-11. S. Gilje, O. Choi, R.B. Kaner, and H.T. Hahn, "Graphite Particle Size Effects on Mechanical Properties of Epoxy Composites," *SAMPE 2006 Proc.* (CD ROM), May 2006.

Exfoliated graphite has come into favor as a filler material for epoxy composites because of the strong sp^2 bonding within a single graphene layer, coupled with the low cost of graphite. Thus far, the challenge in using graphite as a filler material has been exfoliating the layers of graphite in order to achieve very thin platelets with high aspect ratios. Exfoliation allows the platelets to be easily dispersed providing the maximum efficiency for a given volume percentage. In our work, we investigate the effect of graphite plate diameter on the mechanical properties of a finished exfoliated graphite/epoxy composite. We first mill the graphite to the desired plate diameter and characterize using dynamic light scattering particle size analysis, and scanning electron microscopy. The graphite is then intercalated using potassium to form the potassium-graphite intercalation compound KC_8 , which is subsequently exposed to methanol and rapidly heated using microwave irradiation to induce exfoliation. The treated graphite is then incorporated into an epoxy matrix using 1 vol. % of exfoliated graphite to epoxy resin. The composites are characterized using three-point bend flexural testing of the mechanical properties.

- C-12. H. Kim, H.T. Hahn, L.M. Viculis, and R.B. Kaner, "Graphite Nanoplatelet (GNP)/Polymer Nanocomposites based on Potassium-Benzene-Intercalation Compounds," *Proc. American Society for Composites, 21st Technical Conference* (CD ROM), Sept. 2006.

Graphite nanoplatelet (GNP)/polymer nanocomposites using potassium-benzene intercalation compounds (K-benzene-GICs) were prepared by *in situ* exfoliation polymerization. Graphite nanoplatelets were intercalated with potassium (K) at an elevated temperature in vacuum to form potassium-intercalation compounds (KGICs) of the first stage, KC_8 . KC_8 GICs were then reacted with benzene at an elevated temperature in vacuum to allow the formation of benzene oligomers in the interlayer galleries. The synthesized KC_8 -benzene compounds were used to manufacture KC_8 -benzene/polymer nanocomposites: KC_8 -benzene/polystyrene (PS), KC_8 -benzene/vinyl ester, and KC_8 -benzene/epoxy nanocomposite. The micro- and nanostructures of KC_8 -benzene/polymer nanocomposites were investigated using high resolution transmission electron microscopy (HRTEM), scanning electron microscopy (SEM), and X-ray diffraction (XRD). KC_8 -benzene/polymer nanocomposites showed the presence of very small graphite crystallites in XRD analysis, indicating the original GNPs were delaminated into a large number of crystallite sheets after the *in situ* polymerization of matrix resin in the interlayer galleries. TEM micrographs show these crystallite sheets consisting of only a few graphene layers as a result of exfoliation polymerization. SEM micrographs indicate well-dispersed graphite crystallites in KC_8 -benzene/PS nanocomposite. These results indicate that benzene intercalation into KC_8 as a secondary intercalant helped the other monomer molecules penetrate into the interlayer galleries to polymerize. The present results indicate that polymer nanocomposites with well-dispersed, thin graphite nanoplatelets can be manufactured using KC_8 -benzene intercalation compounds through *in situ* exfoliation polymerization.